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# Nickel oxide reduction studied by environmental TEM and *in situ* XRD

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Nickel oxide reduction and subsequent Ni behaviour under  $H_2$  is of practical importance in the field of solid oxide fuel cell (SOFC) technology, as it determines the structure of the electronic conductor on the anode side during operation [1]. Despite extensive coverage in the literature [2], several questions remain, notably regarding the NiO reduction kinetics and its structural evolution.

Here, we perform *in situ* reduction of an industrial NiO powder from JT Baker<sup>TM</sup> under 1.3 mbar of  $H_2$  (2 ml<sub>N</sub>/min) in a differentially pumped FEI Titan environmental transmission electron microscope (ETEM) [3]. Images, diffraction patterns and electron energy-loss spectra are acquired during different temperature ramps (300 to 600°C) in order to monitor the structural and chemical evolution of the system. Similar experiments are performed in a PANalytical X'Pert PRO X-ray diffractometer equipped with an Anton Paar furnace and a mass spectrometer to complement and extrapolate the ETEM data to higher pressures and gas flows. Diffraction peak intensities, crystallite sizes (obtained using the Scherrer formula) and  $H_2/H_2O$  mass spectrometer signals are monitored.

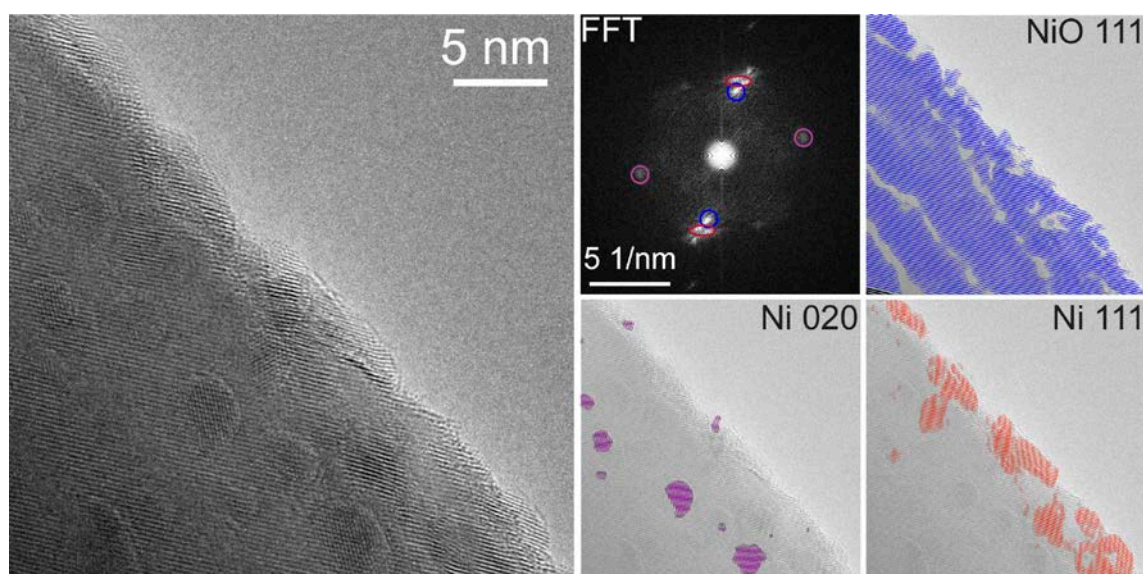
The recorded images and diffraction patterns show that the nucleation of Ni on NiO takes place at temperatures below 400°C and is either epitaxial with a small angle misfit in thin specimen areas (Fig. 1) or randomly oriented in thicker regions. Reduction proceeds through the growth of Ni domains and the movement of interfaces, the latter inducing particle shrinkage and pore creation within larger particles. Densification is observed when the temperature approaches 600°C: the porosity that was created at lower temperatures disappears. This reorganization of Ni is detrimental to the connectivity of the Ni catalyst and to the reduction-reoxidation stability of the SOFC [4].

Reaction kinetics are measured in the ETEM by electron energy-loss spectroscopy using two different techniques based on changes of the Ni  $L_{2,3}$  white lines upon reduction (either taking the ratio of the Ni  $L_3$  and  $L_2$  integrated intensities or using multiple linear least squares fitting of NiO and Ni experimental reference spectra [5,6]). Reduction starts earlier but at a higher temperature when the heating rate is increased (380°C at 2°C/min compared to 420°C at 7°C/min). The initiation of the reduction depends on the number of oxygen surface vacancies, which in turn depends on the temperature and time [7]. Reduction proceeds quickly until the remaining NiO fraction reaches a level of about 30% (Fig. 2). The reaction then slows down and full reduction is only achieved at temperatures above 600°C (confirmed using diffraction). This decrease in reaction rate appears to be caused by physical factors, as NiO reduction is known to be autocatalytic [2]. As only a few micrograms of reducible material are dispersed on the TEM grid and considering the volume of the reaction chamber in the ETEM (~800 cm<sup>3</sup>), a shortage of reactive gas is unlikely even in 2 mbar of  $H_2$ . It is probable that the presence and stagnation of  $H_2O$  vapour created upon reduction blocks  $H_2$  access to the reactive sites, decreasing the reaction rate at a high conversion fraction. The gas flow is low and may not evacuate the product gas efficiently around the Ni(O) particles. Complementary XRD experiments point towards the same conclusion and underline the impact of the pressure and gas flow on the kinetics.

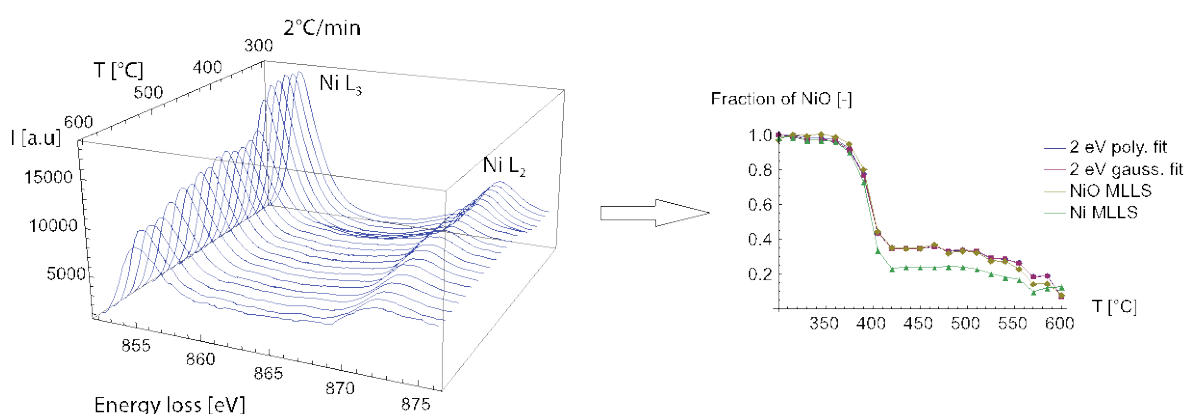
It is possible to determine an approximate activation energy for NiO reduction inside the ETEM using the Kissinger method [8], which is based on measurements of the shift in the temperature at which the reaction rate is maximum for different heating rates. With EELS experiments performed at 2, 4 and 7 °C/min, an activation energy of  $\sim 70 \pm 20$  kJ/mol is obtained, which is consistent with values found in the literature [2].

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**Figure 1.** Ni nucleation on NiO observed using ETEM at 370°C under 1.3 mbar of H<sub>2</sub>. High-resolution (left), FFT (middle top) and inverse FFT (colored) images illustrate the epitaxial growth of Ni on NiO in thin areas (with a small angle misfit resulting in a splitting of the Ni 111 reflections).



**Figure 2.** Evolution of electron energy-loss spectra as a function of temperature (left), used to extract reduction kinetics (right) using the change in the shape of the Ni L<sub>2,3</sub> white lines using either the ratio of the Ni L<sub>3</sub> and L<sub>2</sub> intensities integrated with a 2 eV window (polynomial or gaussian fit for integration) or a multiple linear least squares (MLLS) technique, which fits a given spectrum using NiO and Ni experimental reference spectra.  $I(L_3)/I(L_2)$  ratios lower than in the literature are found as the spectra are not deconvolved to remove plural scattering (specimen thickness is not constant and varies from 50 to > 200 nm) [9].